

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/000224

International filing date: 21 January 2005 (21.01.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0409078.3
Filing date: 23 April 2004 (23.04.2004)

Date of receipt at the International Bureau: 25 February 2005 (25.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



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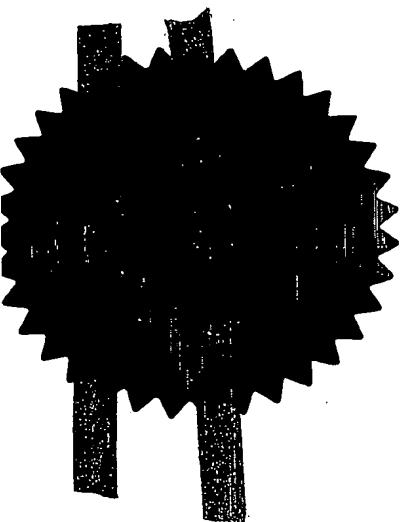
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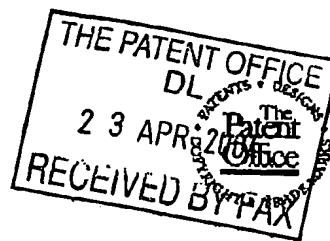
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The Victoria University of Manchester
Oxford Road,
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Patents ADP number (if you know it)

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773945001

4. Title of the invention

Ceramic Coating

5. Name of your agent (if you have one)

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12. Name and daytime telephone number of person to contact in the United Kingdom

Dr. Lucy Tovell

0161 827 9400

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DUPPLICATE

Ceramic Coating

The present invention relates to a ceramic coating and a method of preparing and applying said coating.

Ceramic coatings are typically applied to substrates to provide protection, in particular thermal protection to the underlying substrate. These substrates tend to be metallic.

One desirable method of producing a ceramic coating is by a slurry process.

A slurry process involves preparing either an aqueous or non-aqueous slurry, applying the slurry to the substrate to form a layer or multi layer coating. The coating is then heat treated or sintered in order that a ceramic coating is produced. The coating prior to sintering is referred to as a green coating.

Many ceramic coatings comprise zirconia. However, zirconia is not generally suitable for application to a metallic substrate by a slurry process.

Typical zirconia coatings comprise crystallite of a conventional size typically in the range from about 1 to about 10 microns. In order to produce a ceramic coating these conventional sized zirconias require sintering temperatures of around 1400°C, clearly the metallic substrate cannot withstand such a temperature. Furthermore, the green coating tends to shrink during drying and sintering, causing an uncompromising

dimensional mismatch between the coating and the substrate and thereby leading to the coating cracking and/or spalling.

Therefore, no crystalline ceramic coatings of a thickness greater than 100 μm have been produced by a slurry method.

5 However, ceramic coatings of a thickness greater than 100 μm are routinely utilised as a thermal barrier coating (TBC) in gas turbine engines.

Typically, a thermal barrier coating system comprises of partially stabilised zirconia (PSZ) coat which adheres to the substrate via a layer of Al_2O_3 which is present on the surface of the substrate.

10 However, the use of these thermal barrier coatings is limited by their long-term durability.

Studies have shown that it is essential for TBC's to have a low elastic modulus in the plane of the coating to minimise the development of thermal expansion mismatch stresses and a low thermal conductivity perpendicular to the coating to 15 minimise the heat transport through the coating to the underlying substrate. In order to address this, attempts have been made to control the porosity of the coatings by way of modifying the method of application of TBC's.

Thermal barrier coatings are currently applied by thermal spraying and electron beam physical vapour deposition (EPPVD).

However, whilst these techniques allow variation in the porosity of the coating they are expensive and require high capital investment and high operation cost.

Furthermore, both are so-called light-on-sight techniques. That is, techniques that are only suitable for the application of TBC's to visible areas of a substrate and as 5 such it is impossible to deposit coating material on inner surfaces of deep holes and other hard to reach places.

In an attempt to address the aforesaid problems researchers have turned to nano-size technology. The past decade has seen enormous investment in nano particles and nano-structure technologies. Nano-size technology not only delivers 10 unusual properties and performance of components, but it also provides opportunities to revolutionise material processing techniques.

As mentioned previously conventional size crystalline zirconias are sintered at temperatures around 1400°C. Clearly, it is not possible to sinter such coatings whilst they are in contact with a metallic substrate as the substrate cannot withstand such 15 temperatures.

The use of nano-size zirconias enables the sintering temperature to be reduced to around 975°C. However, this temperature is still too high for some metallic substrates.

Therefore, it is highly desirable to develop a coating and a method for its application which enables ceramic coatings to be sintered when in direct contact with a metallic substrate.

Such a system would reduce the cost of coating a metallic substrate, and offer 5 more flexibility in that a coating could be applied to components with complex geometries.

According to the first aspect of the present invention there is provided a green ceramic coating composition comprising nano-sized particles dispersed within a solvent together with pre-formed particles.

10 According to the second aspect of the present invention there is provided a method for producing a ceramic coating upon a substrate comprising the following steps: preparing a nano-suspension containing nano-sized ceramic particles, preparing pre-formed particles, concentrating the nano-suspension to form a nano-slurry, mixing the preformed particles with the nano-slurry, applying the aforesaid 15 mixture to the substrate, and heat treating the system such that the aforesaid particles become sintered thus producing a ceramic coating.

Advantageously, the composition of the present invention can be used to produce a ceramic coating which does not crack or spall during the drying and sintering procedures. Significantly, the ceramic coating produced from the

composition of the present invention comprises a crystalline nano-structure.

Moreover, the composition of the present invention can be used to produce a coating having a thickness of upto 500 μ m. This thickness may be achieved by the application of one or more layers of the composition of the present invention.

5 Furthermore, the method of the present invention is a non-light-of-sight technique such that all areas, including non-visible areas, of a substrate having a complex geometry may be coated.

A significant advantage of the present invention is that the combination of pre-formed particles with nano-size particles enables the coating composition to be 10 sintered at a lower temperature which a metallic substrate can withstand. This is thought to arise as a result of the lower temperature binding effect of nano-sized particles.

A further advantage of the present invention is that the nano-sized particle structure gives rise to a coating has a low thermal conductivity such that the 15 underlying metallic substrate is protected from heat.

Due to the use of a combination of pre-formed particles and nano-sized particles the morphology and distribution of porosity of the coating can be specifically tailored having regard for the application of the coated substrate.

Nano-sized particles can be synthesised using various techniques, such as chemical precipitation, sol-gel, hydrothermal synthesis, chemical vapour condensation, inert gas condensation, etc.

A nano-suspension can be prepared either by dispersing nano-sized particles 5 within a solvent or applying wet chemical techniques, e.g. hydrothermal methods, which produce a suspension system directly without the necessity of dispersion.

Preferably the preformed particles have a variety of different shapes and these particles may be derived from any suitable ceramic material. The pre-formed particles comprise a crystalline nano-structure.

10 Preferably the size of the nano-sized particles is less than 200nm and more preferably less than 100nm. Advantageously, this smaller particle size provides a better binding effect such that a lower sintering temperature can be utilised to achieve a cohesive coating. Therefore, the nano-sized particles of the present invention preferably have a narrow particle size distribution, typically in the range from 10nm

15 to 100nm.

The solvent of the present invention is preferably water or a polar organic solvent, for example ethanol and isopropyl acetate (IPA).

The nano-sized particles are dispersed in the solvent such that a nano-suspension is afforded. As referred to herein a nano-suspension is a system whereby

the nano-sized particles have a low solid loading, of typically less 10wt%. A nano-slurry as referred to herein is a system whereby the nano-sized particles have a higher solid loading, typically greater than 20wt%.

An important aspect of the present invention is the preparation of the pre-formed particles. Typically these particles have a particle size ranging from 5 μ m to 300 μ m and preferably from 10 μ m to 150 μ m. The nano-structure of the pre-formed particles may comprise crystallites in the order of 100 to 200nm in size.

The pre-formed particles can be prepared using colloidal processing. This approach minimises defects formed by dry powder methods.

10 The pre-formed particles are typically prepared from a nano-suspension or nano-slurry of a suitable ceramic material by known methods such as electrophoretic deposition (EPD), dip coating, blade coating, spray drying and air drying.

Suitable ceramic materials which may used alone or in combination include oxides, borides, silicides, phosphates, sulfides of any of the following species boron, 15 aluminium, silicon, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, lanthanum, yttrium, iron, cobalt and nickel.

In a preferred embodiment of the method of the present invention the pre-formed particles are prepared by air-drying. A concentrated nano-slurry is allowed to dry in air at room temperature to form a solid compact. The solid compact is then

crushed and ground. The ground material is then classified by way of a sieve. The ensuing pre-formed particles are of irregular shape, but are nevertheless broadly equiaxed.

In a further preferred embodiment of the method of the present invention the 5 pre-formed particles are prepared by dip coating a nano-slurry on a substrate, followed by drying and peeling ensuing dried coating from the substrate. The peeled coating is crushed and ground and sieved in order to size classify the pre-formed particles.

In a particularly preferred embodiment of the method of the present invention 10 the pre-formed particles are prepared by a combination of EPD and dip coating. This combination produces pre-formed particles having a plate-like physical form or small hollow tubes.

As varying the geometries of the pre-formed particles results in ceramic 15 coatings having different microstructures and therefore different mechanical and thermal properties the choice of method for preparing the pre-formed particles can be used to influence the properties of the ceramic coating. For example, the thickness and aspect ratio of the plate-like particles can be adjusted by varying the slurry/suspension concentration, deposition time and deposition rate

The present invention adopts a 'bricks and mortar' approach whereby the pre-formed particles are the 'bricks' and the slurry/suspension of nano-sized particles is the 'mortar'.

A key step in the method of the present invention is the concentration of the 5 nano-suspension to a nano-slurry with a desired solid loading. The nano-slurry tends to be in the form of a paste. The nano-suspension is preferably concentrated by way of freeze drying or heat drying in either air or vacuum.

The solid loading of the nano-slurry is preferably 20 to 60 wt%.

The ratio of the pre-formed particles to the nano-sized particles is in the range 10 from 1:5 to 1:1 and preferably is 2:5 on a dry weight basis. Once concentrated, the paste is preferably stored in a sealed container in order that the paste does not dry out prematurely.

In order to aid application of the paste to the substrate and change the rheology of the paste any of the following may be added to the paste either alone or in 15 combination; water, at least one polar dispersing medium such as ethanol and at least one polymeric surfactant/binder. Suitable polymeric surfactants/binders include poly-methacrylic acid (PMAA), poly-methylmethacrylate (PMMA), polyvinyl alcohol and methyl cellulose. Such polymeric surfactants/binders may be added to the paste in quantities upto about 5% w/w. The use of pastes having differently shaped preformed

particles enables the pore architecture of the coatings to be manipulated. Such manipulation leads to distinctive thermal conductivity of the coatings. For example the use of plate-like pre-formed particles produced by EPD gives rise to a coating having a parallel pore structure and a relatively lower thermal conductivity. In contrast to this, the use of pre-formed particles with irregular shapes gives rise to a coating having a random pore structure and therefore a relatively higher thermal conductivity. The coatings of the present invention may have a thermal conductivity less than 1.0 w/m°C and a porosity of more than 30 vol%. Typical plasma sprayed TBC's have been found to have a thermal conductivity of 1.22 w/m°C.

10 It has long been thought that the relatively low thermal conductivity of TBC's produced by PS and EBPVD techniques is due to the meta-stable tetragonal phase of zirconia present in the coating. However, the coatings of the present invention comprise only stable phases i.e. tetragonal and cubic phases. Thus, the coatings have no meta-stable phase, but still have a lower thermal conductivity than plasma sprayed

15 coatings.

The coating composition of the present invention may be used to provide a multi-layered ceramic coating. Furthermore, each coat may comprise pre-formed particles having different architecture. For example, a paste comprising pre-formed particles having a plate like structure may be applied to a substrate and following heat

treatment of that paste a second paste comprising irregularly shaped pre-formed particles may be applied thereto and heat treated

The green coating of the method of the present invention may be heat treated at any temperature in the range from 300 to 1200°C. However, heat treatment at 5 500°C produces a ceramic coating which exhibits good strength and adhesion.

In order to increase the coating integrity and improve the coating/substrate adhesion, the coating is preferably infiltrated with an infiltration suspension or slurry after its heat treatment.

Advantageously, this infiltration modifies the porosity of the coating and 10 increases the inter-particle connectivity between the pre-formed particles of the coating.

The infiltration process preferably takes place in a pressure chamber at a pressure preferably greater than 1MPa. However, prior to infiltration the chamber is vacuum-pumped in order to eliminate air and/or absorbed gas species from the pores 15 of the green coating.

The infiltration suspension or slurry may contain exclusively nano-particles or a mixture of nano-particles and conventional fine powders dispersed in water, acetone, acetylacetone or other similar polar solvent. The solid loading of the infiltration suspension or slurry is preferably in the range from 5 to 80wt%.

Once infiltrated, the coating is then dried and heat treated at a temperature in the range from 500 to 1200°C, either in a vacuum or in air.

The infiltration process and subsequent heat treatment may be repeated until the desired density and architecture are achieved.

5 In order that the present invention be more readily understood the present invention will now be described by way of example only and with reference to the following examples and drawings in which:

10. Figure 1 shows a representation of irregular pre-formed particles prepared in accordance with one embodiment of the present invention;

Figure 2 shows a representation of plate-like preformed particles prepared in accordance with one embodiment of the present invention;

15 Figure 3 is a graph showing the thermal diffusivity of a variety of coatings having differing pore structures;

Figure 4 is a graph showing the thermal conductivity of a variety of coatings according to the present invention, said coatings having differing pore structures;

Figure 5 is a graph showing the effects of infiltration on the porosity of the coating.

Figure 1 shows the irregularly shaped pre-formed particles that are typically produced by air-drying.

5 Figure 2 shows the plate-like pre-formed particles that are typically produced by EPD coating.

Figure 3 shows how the porosity of the coating changes the thermal diffusivity of the coating. It can be seen that the coating with random pore structure has a similar thermal diffusivity to that of plasma-sprayed coating, while the coating with parallel pore structure has a much smaller thermal diffusivity. Measured by mercury porosimeter, the plasma sprayed coating was found to have 18% porosity, the coating with random pore structure had 28% porosity, and the coating with parallel pore structure had 30% porosity. Therefore, thermal diffusivity is dependent mainly on pore structure, while porosity does not seem to have an influence on thermal diffusivity.

10 15 Figure 4 shows how the porosity of the coating changes the thermal conductivity of the coating. It can be seen that the coating with random pore structure has a lower thermal conductivity than that of plasma-sprayed coating while the thermal conductivity of the coating with parallel pore structure is only about a quarter

of that of plasma sprayed coating. Therefore the thermal conductivity is dependent not only on pore structure, but also on porosity.

Figure 5 shows how infiltrating the coating changes the porosity of the coating. It can be seen that as more infiltration is carried out on the coating, the less 5 porous the coating is. Also it appears that large pores are the first to be filled by infiltration, indicating that the porosity distribution can be modified by the infiltration operation.

EXAMPLE 1

An aqueous nano-suspension of ZrO_2 doped with 5.3wt% Y_2O_3 and 0.25wt% 10 Al_2O_3 was used as the starting material. The original nano-slurry of 24wt% in solid load concentration was diluted with distilled water to 3wt% in solid loading. EPD was employed for the preparation of plate-like pre-formed particles. For EPD, an electrical field of 3-5volt/cm and deposition time of 2-5 minutes were used. The deposited layer obtained as such was about 5-10 μm in thickness. Upon crushing and 15 sieve classification, plate-like particles of 5~20mm in thickness and 50~250mm in length were obtained. Further on heat treatment at 1200°C, the plate-like particles were consolidated to dense entities. A paste was prepared by mechanically blending of 5 grams of plate-like particles with 5 grams of nano-slurry for which the solid loading is 53wt%. The paste was plastered onto Fecrialloy substrate. After being dried 20 at room temperature and heat treated at 1200°C for 1h in air, coating pre-forms of 100~500mm in thickness were obtained with good integrity. The plate-like particles were found to be predominately oriented in parallel to the substrate. The pre-forms

were further subjected to infiltration with a nano-slurry of 48wt% in solid loading, under a pressure of 1 MPa and heat treatment at 800°C. The infiltration and subsequent heat treatment were repeated for twice and finally the coatings were sintered at 1200°C for 1h.

5 EXAMPLE 2

The same procedure was followed as in sample 1, except that the first time heat treatment was conducted at 500°C and final sintering was conducted at 1100°C; and the repetition of the infiltration and heat treatment was five times.

EXAMPLE 3

10 The same procedure was followed as in sample 1, except that the stainless steel substrate was used and first time heat treatment was conducted at 500°C, and final sintering was conducted at 900°C and the repetition of the infiltration and heat treatment was five times.

EXAMPLE 4

15 The same procedure was followed as in sample 1, except that the pre-formed particles were in irregular shape which was statistically equiaxed, the size of the preformed particle was 10~100mm.

EXAMPLE 5

An aqueous nano-suspension of ZrO_2 doped with 8wt% Y_2O_3 was used as the 20 starting material.

The original suspension (23wt%) was diluted with distilled water to 5~10 wt% in solid loading.

EPD was employed for the preparation of plate-like preformed particles. For EPD, an electrical field of 5volt/cm and deposition time of 2~5 minutes were used.

The deposited layer obtained as such was about 5~10mm. Upon crushing and sieve classification, plate-like particles of 30~150mm in length and 5~10mm in thickness were obtained. Further on heat treatment at 1200°C, the plate-like particles were consolidated to dense entities. A paste was prepared by mechanically blending of 3 grams of plate-like particles with 3 grams of nano-slurry for which the solid loading is 57wt%. The paste was plastered onto FeCrAlloy substrate. After being dried at room temperature and heat-treated for the first time at 1030°C for 1h in vacuum ($<10^{-5}$ Torr), coating pre-forms of 100~500mm in thickness were obtained with good integrity. The plate-like particles were found to be predominately oriented in parallel to the substrate. The pre-forms were further subjected to infiltrating with a nano-slurry of 40~60wt% in solid loading, under a pressure of 1 MPa and heat treatment at 1030°C in vacuum ($<10^{-5}$ Torr). Finally the coatings were sintered at 1200°C in air for 1h.

EXAMPLE 6

15 The same procedure was followed as in sample 5, except that the first time heat treatment was conducted at 500°C in air, and the repetition of the infiltration and heat treatment was five times.

EXAMPLE 7

15 The same procedure was followed as in sample 5, except that the pre-formed 20 large particles were in randomly irregular shape, the size of the pre-formed particle was 10~45 mm. For the preparation of the paste, 8 grams of large particles was mixed with 4 grams of nano-slurry for which the solid loading was 57wt%.

EXAMPLE 8

The same procedure was followed as in sample 7, except that the size of the pre-formed particle was 10-75 mm.

EXAMPLE 9

5 The same procedure was followed as in sample 7, except that 5 grams of large particles was mixed with 5 grams of nano-slurry for which the solid loading was 57wt% for the preparation.

EXAMPLE 10

10 The same procedure was followed as in sample 7, except that an acetylacetone based ZrO_2 suspension was used for infiltration, which was obtained by attrition milling of ZrO_2 (with 8wt% Y_2O_3) powder in acetylacetone for 64 hours.

15 It is of course to be understood that the present invention is described by way of example only and is not intended to be restricted to the above examples and embodiments.

CLAIMS

1. A green ceramic coating composition comprising nano-sized particles dispersed within a solvent together with pre-formed particles.
2. A coating composition according to claim 1, wherein the pre-formed particles have a crystalline nano-structure
3. A coating composition according to claim 1 or claim 2, wherein the nano-sized particles are less than 200nm in size.
4. A coating composition according to claim 3, wherein the nano-sized particles are less than 100 nm in size.
5. A coating composition according to claim 4, wherein the nano-sized particles have a particle size distribution in the range from 10nm to 100nm.
6. A coating composition according to any preceding claim, wherein the solvent is selected from water or a polar organic solvent.
7. A coating composition according to any preceding claim, wherein the pre-formed particles have a particle size ranging from 5 μ m to 300 μ m
8. A coating composition according to claim 7, wherein the pre-formed particles have a particle size ranging from 10 μ m to 150 μ m.
9. A coating composition according to any preceding claim, wherein the pre-formed particles are prepared from a ceramic material selected from any of the

following either alone or in combination oxides, borides, silicides, phosphates, sulfides of any of the following boron, aluminium, silicon, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, lanthanum, yttrium, iron, cobalt and nickel.

- 5 10. A method for producing a ceramic coating upon a substrate comprising the following steps: preparing a nano-suspension comprising nano-sized ceramic particles, preparing pre-formed particles, concentrating the nano-suspension to form a nano-slurry, mixing the preformed particles with the nano-slurry, applying the aforesaid mixture to the substrate, and heat treating the system such that the aforesaid particles produce a ceramic coating.
- 10 11. A method according to claim 10, wherein the ratio of pre-formed particles to nano-sized particles is in a range from 1:5 to 1:1 on a dry weight basis.
12. A method according to claim 11, wherein the ratio of pre-formed particles to nano-sized particles is 2:5.
- 15 13. A method according to any of claims 10 to 12, wherein the nano-slurry has a solid loading of from 20 to 60 wt%.
14. A method according to any of claims 10 to 13 wherein the nano-slurry is in the form of a paste.

15. A method according to any of claims 10 to 14, wherein the paste comprises any of the following additional ingredients either alone or in combination: water, at least one polar dispersing medium and at least one polymeric surfactant.
16. A method according to claim 15, wherein the polymeric surfactant is selected from polymethacrylic acid (PMAA), poly-methacrylate (PMMA), polyvinyl alcohol and methyl cellulose.
17. A method according to claim 15 or claim 16, wherein the polymeric surfactant constitutes upto about 5% w/w.
18. A method according to any of claims 10 to 17, wherein the coating afforded has a thermal conductivity below 1.0 w/m°C.
19. A method according to any of claims 10 to 18, wherein the coating afforded comprises stable zirconia phases.
20. A method according to any of claims 10 to 19, wherein the green coating is heated at any temperature in the range from 300 to 1200°C.
- 15 21. A method according to any of claims 10 to 20, wherein following heat treatment the ceramic coating is infiltrated with an infiltration suspension or slurry.
22. A method according to claim 21, wherein the infiltration process takes place in a pressure chamber at a pressure greater than 0.1 MPa.

23. A method according to claim 21 or claim 22, wherein the infiltration suspension or slurry exclusively comprises nano-sized particles.
24. A method according to claim 21 or claim 22, wherein the infiltration suspension or slurry comprises a mixture of nano-particles and conventional fine 5 powders.
25. A method according to any of claims 21 to 24, wherein the infiltration suspension or slurry has a solid loading in the range from 5 to 80wt%.
26. A method according to any of claims 21 to 25, wherein following infiltration the coating is dried and heat treated at a temperature in the range from 500 to 1200°C.

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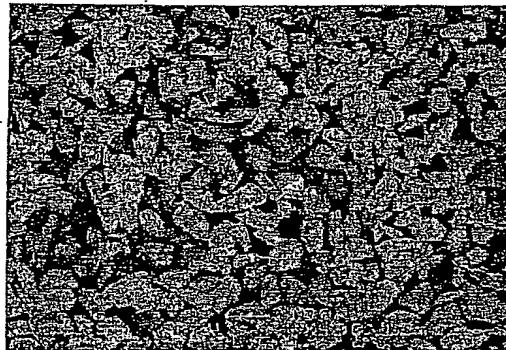


Fig. 1

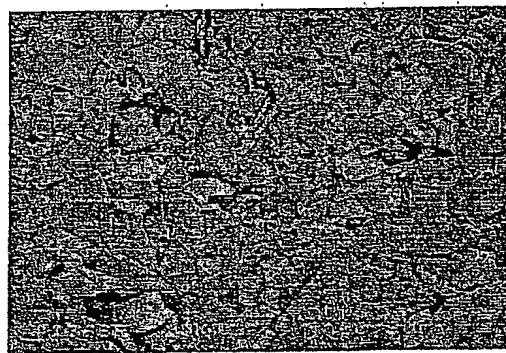


Fig. 2.

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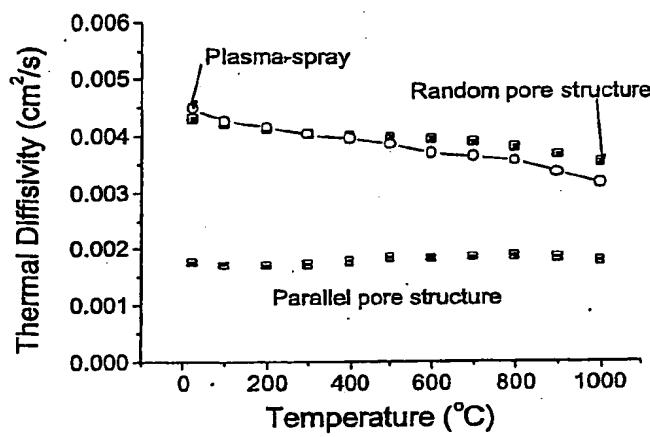


Fig. 3

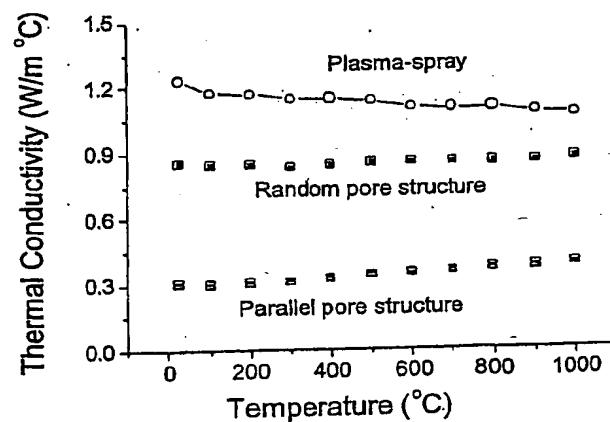


Fig. 4

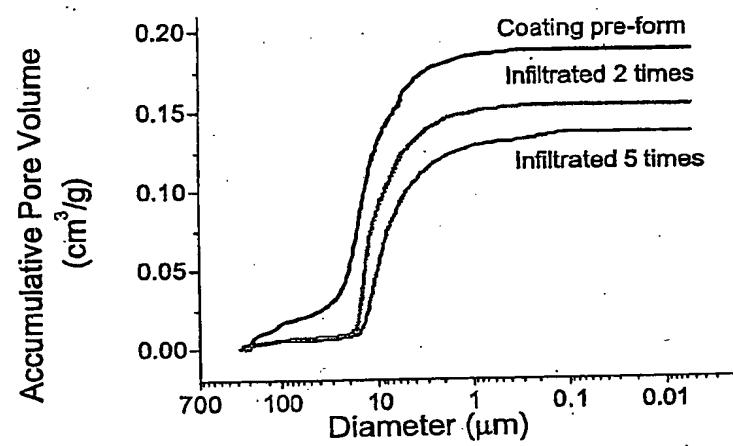


Fig. 5